

A Spectrophotometric Study on Uranyl Nitrate Complexation to 150 °C

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Abstract The formation constant of the mononitratouranyl complex was studied spectrophotometrically at temperatures of 25, 40, 55, 70, 100 and 150 °C (298, 313, 328, 343, 373 and 423 K). The uranyl ion concentration was fixed at approximately $0.008 \text{ mol}\cdot\text{kg}^{-1}$ and the ligand concentration was varied from 0.05 to $3.14 \text{ mol}\cdot\text{kg}^{-1}$. The uranyl nitrate complex, UO_2NO_3^+ , is weak at 298 K but its equilibrium constant (at zero ionic strength) increases with temperature from $\log_{10} \beta_1 = -0.19 \pm 0.02$ (298 K) to 0.78 ± 0.04 (423 K).

Keywords Stability constants · Uranyl nitrate · Spectrophotometric · Aqueous solution

1 Introduction

Uranyl ion and its complexes with various ligands plays an important role in the extraction and beneficiation chemistry of uranium. Quantitative modeling of these processes as well as the modeling of the other chemical, geological and biological processes involving uranium requires knowledge of reliable thermodynamic complexation constants. Recently, the study of uranyl complexes with inorganic ligands such as Cl^- , CO_3^{2-} , SO_4^{2-} and NO_3^- in aqueous solutions at elevated temperatures has undergone renewed interest because of the importance of uranium solution chemistry and mobility in nuclear waste disposal environments. Available literature data on uranyl complexation constants with nitrate ion suffer from inconsistency and are limited to only low temperature ambient conditions.

The interaction between UO_2^{2+} and NO_3^- is weak, with reported values for the apparent equilibrium constant for UO_2NO_3^+ formation [1–9] ranging from 0.04 to 0.63 at 25 °C (Table 1, Refs. [2, 3, 5, 8]). The large scatter reflects the difficulty in determining the stability of weak complexes, often with inappropriate methods. Of particular interest is the study by Brooker et al. [9] whose Raman spectroscopic measurements of uranyl nitrate complexation in aqueous nitrate media provide evidence for the formation of only one complex, UO_2NO_3^+ ,

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Table 1 Thermodynamic data for the reaction $\text{UO}_2^{2+}(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightleftharpoons \text{UO}_2\text{NO}_3^+(\text{aq})$ where Q is the apparent equilibrium constant

$t/^\circ\text{C}$	Medium ^a	Q	Method ^b	Reference
20	1 M NaClO ₄	0.50	Emf	Ahrland [1]
25	5.38 M (Na ⁺ , H ⁺)(ClO ₄ ⁻ , NO ₃ ⁻)	0.21	spec	Betts and Michels [2]
	7.0 M (Na ⁺ , H ⁺)(ClO ₄ ⁻ , NO ₃ ⁻)	0.27		
10	2 M NaClO ₄	0.30	dist	Day and Powers [3]
25		0.24		
40		0.17		
32	1 M NaClO ₄	0.04	exch	Banerjee and Tripathi [4]
25	0.54 M (Na ⁺ , H ⁺)(ClO ₄ ⁻ , NO ₃ ⁻)	0.37	Emf	Ohashi and Morozumi [5]
	0.82 M (Na ⁺ , H ⁺)(ClO ₄ ⁻ , NO ₃ ⁻)	0.20		
	1.06 M (Na ⁺ , H ⁺)(ClO ₄ ⁻ , NO ₃ ⁻)	0.19		
20	8 M HClO ₄	2.94	dist	Lahr and Knock [6]
22	0 M (NaClO ₄)	0.25	spec	Marcantonatos et al. [7]
	2 M (NaClO ₄)	0.29		
25	0.71 M HClO ₄	0.63	dist	Pushlenkov et al. [8]
23	6.25 M (Na ⁺ , H ⁺)(ClO ₄ ⁻ , NO ₃ ⁻)	0.15	spec	Brooker et al. [9]
30	3 M HNO ₃	0.33	Emf	Guorong et al. [22]

^aM denotes units of mol·L⁻¹

^bAbbreviations used are: Emf, potentiometric; spec, spectroscopic; dist, liquid-liquid distribution (water/organic phase); exch, ion exchange

over the entire ligand concentration range to 6.25 mol·kg⁻¹. The aim of this study has, therefore, been to study the formation of the mononitratouranyl complex over a wider range of temperature from 25 to 150 °C at pressures from 1 to 4 bar.

2 Experimental Part

The water used for all experiments was first passed through a Milli-Q reagent grade mixed-bed ion-exchange column and then double distilled in quartz glass. The resistivity of the water was 18.2 MΩ·cm. Nitric acid was used without further purification. Uranyl nitrate hexahydrate (Fishers 99%) was purified by slow recrystallization from dilute solutions of nitric acid. An approximately 0.05 mol·kg⁻¹ uranyl nitrate stock solution was prepared by adding the purified salt to nitric acid. The uranium concentration in the stock solution was determined gravimetrically using 8-hydroxyquinoline as described by Vogel [10]. Thirteen solutions were prepared by quantitative dilution of the uranium containing stock solution with nitric acid. The uranyl concentration after dilution was approximately 0.008 mol·kg⁻¹ and the ligand concentrations were varied from 0.05 to 3.14 mol·kg⁻¹. The total anion concentration (i.e., NO₃⁻) in the working solutions was determined by passing weighed aliquots of the solutions through an ion-exchange resin and titrating the eluents with a standard solution of sodium hydroxide.

The UV-Vis spectra were measured at various temperatures with a double beam Cary 5 UV-Vis spectrophotometer in a thermostatted flow-through fused silica cuvette (Hellma AG) with a 1 cm optical path. Digital spectra were obtained at 0.2 nm intervals with a slit width

of 1 nm. Temperatures were controlled to $\pm 0.005^\circ\text{C}$ with separate Sodev CT-L circulating baths and monitored with calibrated thermistors. At 100 and 150°C , a slight overpressure of nitrogen gas was applied by means of a titanium separator with a movable piston in order to prevent boiling of the solutions.

3 Computational Method

The digital spectra recorded for different wavelengths and different solutions can be represented by an $m \times n$ matrix, \mathbf{A} , where m is the number of data points (i.e., absorbance at specific wavelengths) and n is the number of solutions. Assuming the validity of Beer's law, we can write

$$\mathbf{A} = l\boldsymbol{\varepsilon}\mathbf{C} \quad (1)$$

where l is an optical path length (1 cm), $\boldsymbol{\varepsilon}$ is the $m \times j$ matrix of molar absorptivities, \mathbf{C} is the $j \times n$ matrix of concentrations on the molar scale, and j is number of the absorbing species in solution. At this point, generally speaking, we do not know either $\boldsymbol{\varepsilon}$ or \mathbf{C} . If the chemical model for the processes taking place in the system is known, we can calculate the matrix of concentrations by solving mass action and mass balance equations and then obtain molar absorptivities for the individual absorbing species that are columns of the matrix $\boldsymbol{\varepsilon}$. On the other hand, any real rectangular matrix can be represented by the following relation using singular value decomposition (SVD) [11]

$$\mathbf{A} = \mathbf{U}\mathbf{D}\mathbf{V}^T \quad (2)$$

where $\mathbf{U}(m \times n)$ and $\mathbf{V}(n \times n)$ are matrices with orthogonal columns and \mathbf{D} is the diagonal matrix of singular values. SVD is a widely used technique in statistics, image and signal processing, and pattern recognition. The SVD provides not only a numerically robust solution to the least-squares problem, but it is also directly related to the principle component analysis [12]. Applying principal components analysis (PCA) to the absorbance matrix, \mathbf{A} , we choose a new coordinate system for the data set such that the greatest variance by any projection of the data set lies on the first axis (then called the first principal component), the second greatest variance on the second axis, and so on. The singular values can be used to determine the effective rank of a matrix, \mathbf{A} , and hence the number of absorbing species in the system necessary for the construction of the chemical model. This is facilitated using the Factor Indication Function (IND) [13],

$$\text{IND} = \frac{\text{RSD}(k)}{(n - k)^2} \quad (3)$$

where $\text{RSD}(k)$ is the Residual Standard Deviation [14] calculated from the misfit of the product $\mathbf{U}_{m \times r}\mathbf{D}_{r \times r}\mathbf{V}_{n \times r}^T$ for any first r vectors to the raw absorbance data. The inverse of this function typically reaches a sharp maximum at the optimal value of r , thus indicating the number of absorbing species in the system. If we focus only on these r significant singular values, we can represent the absorbance matrix, \mathbf{A} , in the form,

$$\mathbf{A} = \mathbf{U}\mathbf{D}\mathbf{V}^T + \mathbf{E} \quad (4)$$

where the diagonal matrix, \mathbf{D} has now the $r \times r$ dimension and the matrix \mathbf{E} contains experimental noise. The advantage of the SVD lies in the decreasing dimensionality of the

original vector space and the filtering out of the random noise. Combining Eqs. 1 and 4 and discarding the random noise term, we can write

$$\mathbf{UDV}^T = l\epsilon\mathbf{C}. \quad (5)$$

By introducing the square rotation matrix, $\mathbf{R}(r \times r)$, we can relate the abstract orthogonal matrices, \mathbf{U} and \mathbf{V} , to the desired matrix of absorptivity and the matrix of concentrations as follows:

$$\mathbf{UDRR}^{-1}\mathbf{V}^T = l\epsilon\mathbf{C} \quad (6)$$

and hence

$$\mathbf{UDR} = l\epsilon \quad (7a)$$

$$\mathbf{R}^{-1}\mathbf{V}^T = \mathbf{C}. \quad (7b)$$

The latter over-determined system of linear equations can be solved in a linear least-squares sense, providing knowledge of the concentration matrix, which is in turn determined by equilibrium constants defined by the chemical model. The formation constants for each temperature were optimized with this approach by minimizing the reduced χ^2 (Bevington and Robinson [15]) of $|\mathbf{U}_{m \times r} \mathbf{D}_{r \times r} \mathbf{V}_{n \times r}^T - \epsilon \mathbf{C}|$ of all the spectrophotometric measurements by the Levenberg-Marquardt technique [16]. Once optimum values for \mathbf{R} are known, the calculation of the molar absorptivity matrix, ϵ , is straightforward according to Eq. 7a. Standard deviations were then estimated using the method of the parabolic expansion of χ^2 about the minima using the numerical second derivatives (e.g., Ref. [15]). All calculations were carried out in the computational language of Matlab 7.0.

4 Results and Discussion

The raw spectra at 25 °C, corrected for the background nitrate absorbance, are shown on Fig. 1. Thermal and chemical equilibria were confirmed in all solutions by repeated scans until the spectra remained unchanged. At first glance, the spectra resemble the absorbance of the pure uranyl ion. However, the same spectra normalized for the total uranyl ion concentration as shown in Fig. 2 provide evidence of complexation of the uranyl ion by nitrate, as manifested by an increase in the intensity and a small shift of the absorbance envelope in the 410 to 470 nm region towards longer wavelengths as the ligand concentration increases.

Increasing the temperature drastically diminishes the fine structure features as shown on the Fig. 3 and gives rise to a further increase of the uranyl ion complexation with nitrate. To quantify these effects, we first have to construct a chemical model for the reactions taking place in this system. The first step is to determine the number of absorbing species. This is done by analyzing the Factor Indication Function as mentioned in the previous section. The inverse IND function applied to the spectra of the solutions in the visible wavelength region (360 to 500 nm) shows a sharp maximum at $k = 2$ species at all studied temperatures (Fig. 4). This strongly suggests the presence of only two absorbing species, which can be ascribed to UO_2^{2+} and the first complex UO_2NO_3^+ (also confirmed by the Raman study of Brooker [9]) the formation of which is defined by Eq. 8,



Fig. 1 Background corrected spectra at 25 °C for a series of uranyl nitrate solutions with nitrate concentrations ranging from 0.037 mol·kg⁻¹ (solution a) to 3.12 mol·kg⁻¹ (solution m)

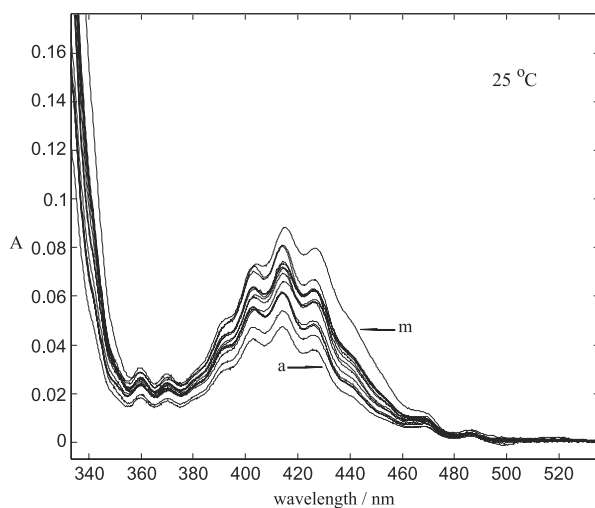


Fig. 2 Spectra (25 °C) normalized to a constant UO_2^{2+} concentration of 0.007 mol·kg⁻¹ for a series of solutions having nitrate concentrations ranging from 0.03 to 3.12 mol·kg⁻¹

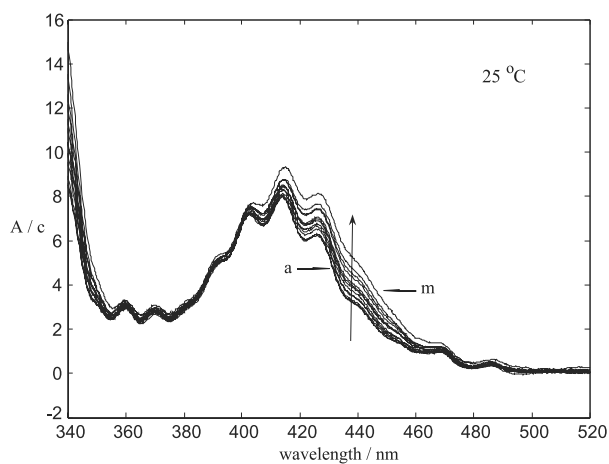


Fig. 3 Temperature dependence of absorption spectra having a uranyl concentration of 0.0088 mol·kg⁻¹ and nitrate concentration of 0.483 mol·kg⁻¹

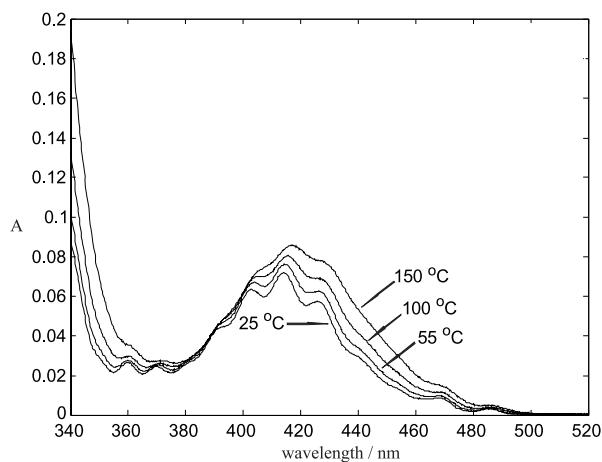
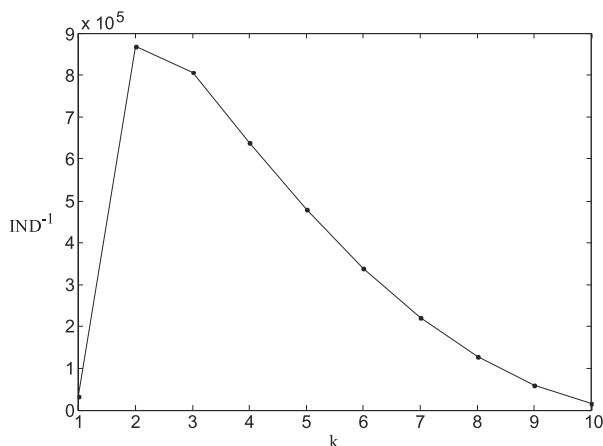


Fig. 4 The inverse IND function applied to the spectra demonstrates two absorbing species in the system



Now that the number and nature of the absorbing species are defined, the relevant mass action and mass balance equations may be solved in order to obtain the equilibrium constants. In this case, the following system of equations needs to be solved:

$$\beta_1 = \frac{M_{\text{UO}_2\text{NO}_3^+} \gamma_{\text{UO}_2\text{NO}_3^+}}{M_{\text{UO}_2^{2+}} M_{\text{NO}_3^-} \gamma_{\text{UO}_2^{2+}} \gamma_{\text{NO}_3^-}} \quad (9)$$

$$M_{\text{UO}_2}^{\text{total}} = M_{\text{UO}_2^{2+}} + M_{\text{UO}_2\text{NO}_3^+} \quad (10)$$

$$M_{\text{NO}_3}^{\text{total}} = M_{\text{NO}_3^-} + M_{\text{UO}_2\text{NO}_3^+} \quad (11)$$

where β_1 is the thermodynamic equilibrium constant for the reaction 8, γ_i is the activity coefficient for the species i and M_i is molarity of this species in solution. Activity coefficients of the individual ions were assumed to have the following form according to the Bronsted-Guggenheim-Scatchard approach [17–19]

$$\log_{10} \gamma_i = -z_i^2 D + \sum_k \psi(i, k) I \quad (12)$$

where D is the Debye-Hückel term:

$$D = \frac{A\sqrt{I}}{1 + B\bar{a}\sqrt{I}} \quad (13)$$

A and B are temperature dependent constants, z_i is the ion charge, I is ionic strength, \bar{a} is the effective diameter of the hydrated ion and $\psi(i, k)$ is the ion interaction parameter between ions i and k . For this study, the term $B\bar{a}$ in the denominator of the Debye-Hückel term has been assigned a value of 1.5 as proposed by Scatchard [18]. Substituting Eq. 12 into Eq. 9 and combining the ion interaction coefficients, we obtain after minor rearrangement:

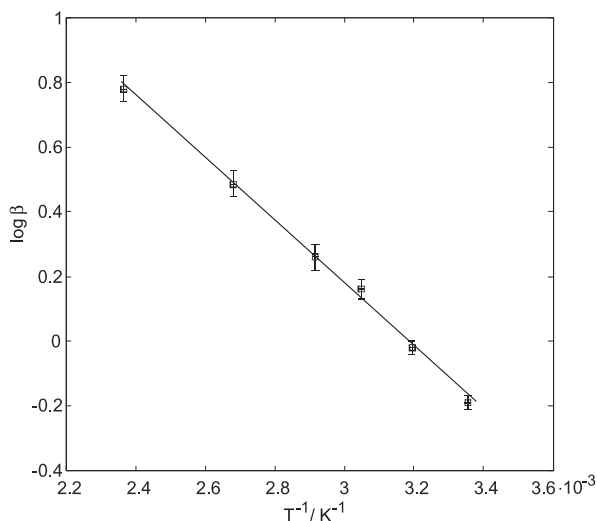
$$\log_{10} \left(\frac{M_{\text{UO}_2\text{NO}_3^+}}{M_{\text{UO}_2^{2+}} M_{\text{NO}_3^-}} \right) + 4D = \log_{10} \beta_1 + bI \quad (14)$$

Table 2 The thermodynamic equilibrium formation constant for the reaction 8 at 1 bar for 25 to 70 °C and at 4 bar for the 100 to 150 °C temperature range; b is overall Debye-Hückel interaction parameter defined in Eq. 14; and Q is the apparent equilibrium constant

$t/^\circ\text{C}$	$\log_{10}\beta_1$	b	Q at $I = 1^a$	Q at $I = 3^a$
25	-0.19 ± 0.02	0.05 ± 0.01	0.11	0.09
40	-0.02 ± 0.02	0.09 ± 0.02	0.17	0.17
55	0.16 ± 0.03	0.12 ± 0.03	0.26	0.30
70	0.26 ± 0.04	0.17 ± 0.03	0.34	0.49
100	0.49 ± 0.04	0.20 ± 0.04	0.53	0.85
150	0.78 ± 0.04	0.24 ± 0.04	0.81	1.47

^aUnits of I : $\text{mol}\cdot\text{L}^{-1}$

Fig. 5 van't Hoff plot of the experimental formation constants



where the single parameter b accounts for the concentration dependence of the apparent equilibrium constant, $Q = \frac{M_{\text{UO}_2\text{NO}_3^+}}{M_{\text{UO}_2^{2+}} M_{\text{NO}_3^-}}$. Considering β_1 and b as being two independent variables, we can simultaneously solve Eqs. 14, 10 and 11 for the molar concentration of all species in solution. Molal to molar concentration scale conversion was based on the density of aqueous solutions of nitric acid and uranyl nitrate [20, 21]. At temperatures greater than 80 °C, the densities of nitric acid solutions were calculated from the relation given by Granzhan and Laktionova [20], which gives densities very similar to those reported by Patterson and Woolley [23] up to 95 °C at $p = 0.35$ MPa. After that is done, it is possible to construct the objective function and find the minimum as described in the previous section. The results of the calculations are summarized in Table 2 and shown as a van't Hoff plot in Fig. 5.

The molar absorptivities of the UO_2^{2+} and UO_2NO_3^+ are shown in Figs. 6 and 7, respectively. Increasing the temperature causes a pronounced increase of intensity and fine structure smoothing for both species UO_2^{2+} and UO_2NO_3^+ . The contribution of the two absorbing species to the total solution absorbance at two arbitrary chosen concentrations are shown on Fig. 8 at 25 and 150 °C. Intermediate spectra were omitted for the sake of clarity. The absorption intensities are typical for spin allowed but Laporte forbidden electronic transitions. The formation of the asymmetric UO_2NO_3^+ complex results in a partially Laporte

Fig. 6 Molar absorptivity of the UO_2^{2+} ion in the temperature range 25 to 150 °C

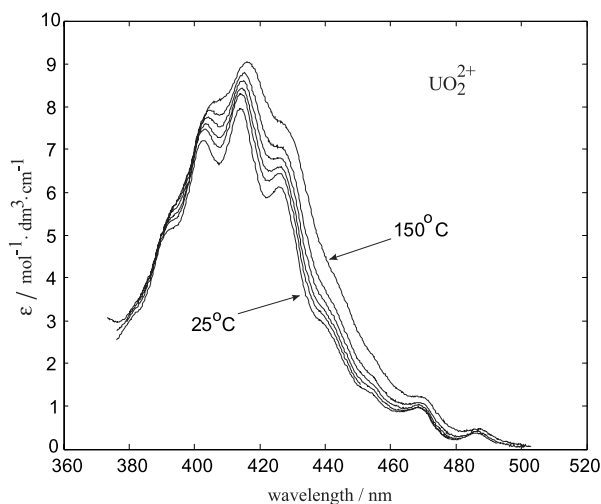
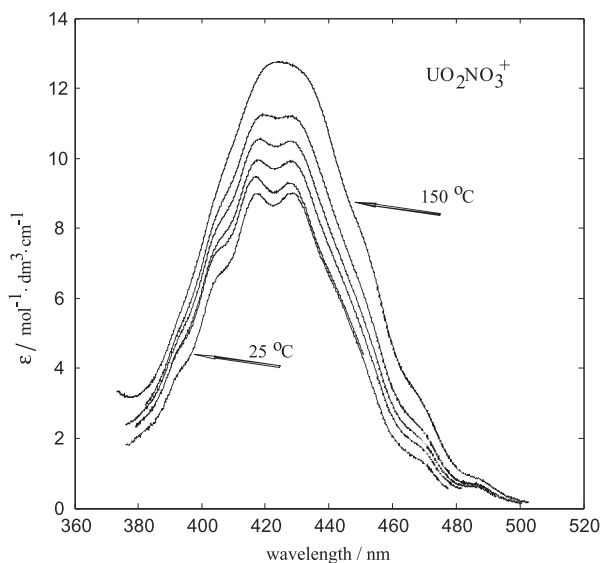


Fig. 7 Molar absorptivity of the UO_2NO_3^+ in the temperature range 25 to 150 °C



allowed transition due to vibronic coupling, and hence results in an increase of the transition intensity.

Finally, the enthalpy and entropy of the complex formation reaction were extracted from the temperature dependence of the equilibrium constants by fitting the equilibrium constants by the following expression,

$$-\log_{10} \beta = \frac{A}{T} + B \quad (15)$$

where A , B are the coefficients of the fit and T is the temperature in K. From Eq. 15, ΔH_{298} and ΔS_{298} for the complex formation reaction can be easily obtained through

$$\Delta H_{298} = 2.303RA \quad (16)$$

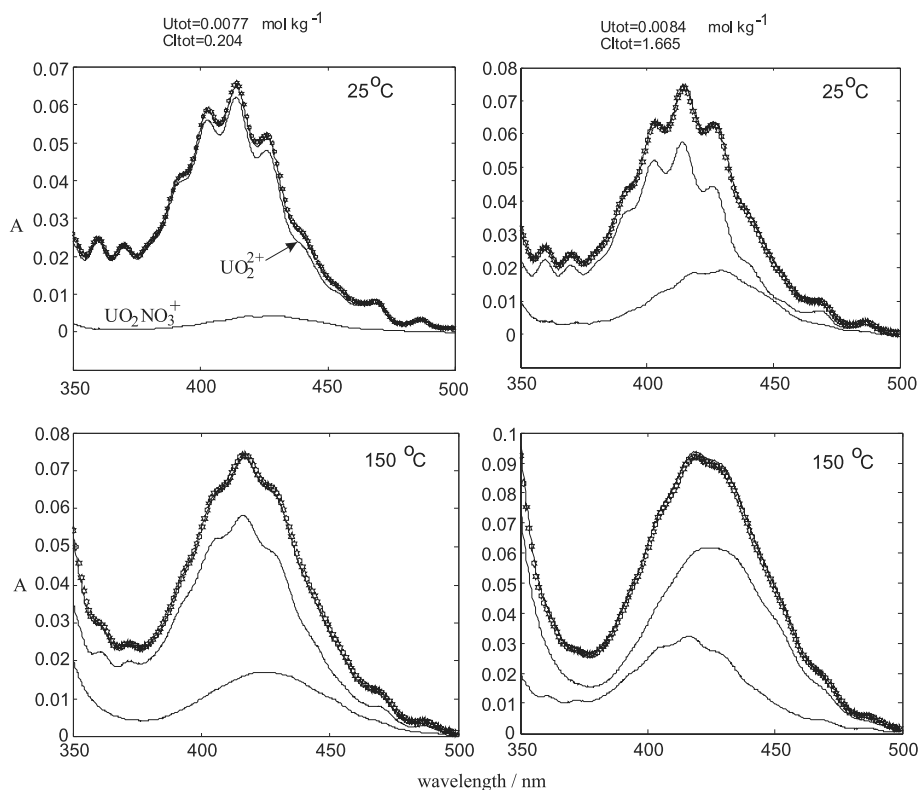


Fig. 8 The contribution of the two absorbing species to the total solution absorbance at 25 and 150 °C

$$\Delta S_{298} = -2.303RB \quad (17)$$

where R is the gas constant. Numerical values for A and B are 969.56 and -3.083 , respectively, which corresponds to the values $\Delta_r H_{298} = 18.5 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_r S_{298} = 59 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ at $I = 0$. Two other studies have reported equilibrium constants for the mononitratouranyl ion obtained as a function of temperature (over the restricted temperature range) and derived enthalpies and entropies for reaction 8. Marcantonatos et al. [7] reported $\Delta_r H_{298}(I = 0) = 3.1 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_r S_{298} = 41 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and Day and Powers [3] reported $\Delta_r H_{298}(I = 2 \text{ mol} \cdot \text{L}^{-1}) = -14 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_r S_{298} = -62 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. However, the thermodynamic data reported from both these studies are considered to be no more than approximate given the notorious unreliability of the van't Hoff isochore approach in deriving enthalpies from equilibrium constant data that extend over a very limited temperature range of only 30 K. The complex formation reaction is endothermic and entropy driven and is similar to those of inner-sphere complexes, which is also confirmed by the Raman study of Brooker et al. [9], where the band 1304 cm^{-1} was associated with monodentate nitrate bonded to the uranyl ion.

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